


Copy 2
National Bureau of Standards
Library, E-01 Admin. Bldg.

MAR 28 1970

NBS TECHNICAL NOTE 513

Hydrogen Fluoride and the Thermochemistry of Fluorine

UNITED STATES
DEPARTMENT OF
COMMERCE
PUBLICATION



U.S.
DEPARTMENT
OF
COMMERCE
National
Bureau
of
Standards

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards¹ was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in four broad program areas. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Measurement Services and the following technical divisions:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic and Molecular Physics—Radio Physics²—Radio Engineering²—Time and Frequency²—Astrophysics²—Cryogenics.²

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; develops, produces, and distributes standard reference materials; relates the physical and chemical properties of materials to their behavior and their interaction with their environments; and provides advisory and research services to other Government agencies. The Institute consists of an Office of Standard Reference Materials and the following divisions:

Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations in the development of technological standards, and test methodologies; and provides advisory and research services for Federal, state, and local government agencies. The Institute consists of the following technical divisions and offices:

Engineering Standards—Weights and Measures—Invention and Innovation—Vehicle Systems Research—Product Evaluation—Building Research—Instrument Shops—Measurement Engineering—Electronic Technology—Technical Analysis.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center consists of the following divisions:

Reactor Radiation—Linac Radiation—Nuclear Radiation—Applied Radiation.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

Information Processing Standards—Computer Information—Computer Services—Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information⁴—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

¹ Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

² Located at Boulder, Colorado 80302.

³ Located at 5285 Port Royal Road, Springfield, Virginia 22151.



TECHNICAL NOTE 513

ISSUED FEBRUARY 1970

Nat. Bur. Stand. (U.S.), Tech. Note 513, 21 pages (Feb. 1970)

CODEN: NBTNA

Hydrogen Fluoride and the Thermochemistry of Fluorine

George T. Armstrong
Physical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

Research supported by the
Air Force Office of Scientific Research
Office of Aerospace Research, U.S. Air Force
under AFOSR Contract No. ISSA. 68-0004

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

Table of Contents

| | Page |
|---|------|
| I. Introduction | 1 |
| Table 1 - Accuracy of Estimates of Heats of Formation of Some Fluorine Compounds | 3 |
| II. Flame Calorimetry of Reactions Forming HF(g) | 4 |
| Table II - Flame Calorimetry Studies of the Heat of Formation of HF(g) | 6 |
| Table III - Some Tabulated Values for $\Delta H_f[\text{HF}]$ | 7 |
| III. Evidence Drawn from Other Reaction Processes | 7 |
| Table IV | 7 |
| Table V - A Series of Reactions Leading to $\Delta H_f[\text{HF(g)}]$ by Hess' Law | 8 |
| Table VI - The Heat of Formation of HF(g) from the Dissociation Energies of H_2 , F_2 , and HF | 9 |
| IV. Recent Work on the Energy of Vaporization from Water | 10 |
| Table VII - Cox and Harrop Study of HF(aq) | 11 |
| Table VIII - Vapor Pressure of HF Over $\text{LiHF}_2(\text{c})$. Effect of a Zero-Point Entropy of $\text{LiHF}_2(\text{c})$... | 12 |
| V. Heat of Formation of Aqueous HF - Recent Studies | 12 |
| VI. New Work on the Dissociation of F_2 and HF | 13 |
| VII. References | 14 |
| VIII. Figures | 17 |

George T. Armstrong

The thermochemistry of hydrogen fluoride is reviewed. The principal emphasis is on the experimental basis of the heats of formation of HF(g) and of HF(aq). Data from flame calorimetry in which HF(g) and HF(aq) are formed, evidence from processes involving other fluorine compounds, and some evidence from spectroscopic and photodissociation studies are brought together.

Key words: Fluorides; fluorine dissociation energy; fluorine thermochemistry; heats of formation; hydrofluoric acid; hydrogen fluoride.

I. Introduction

While it is possible for us to find certain unique features of most elements, in this note we wish only to examine some features of the element fluorine. We may list certain features which make it of special interest:

- (1) It is a cornerstone element. With respect to the periodic system it is in the extreme upper right of the non-noble elements. As a result schemes that correlate properties within period or within group find that in both cases fluorine is the end element. Interpolation is rarely possible; - extrapolation is required in order to obtain properties by estimation.
- (2) It is the most electronegative element and generally conceded to be the most reactive element. Thus bonds of unusual strength are formed to other elements; and most elements are found in compound with it (even some of the inert gases).

The chemistry and many physical properties of fluorine compounds are, therefore, frequently of interest as illustrations (paradigms) of these properties as found among all compounds. The thermochemistry of fluorine surely falls in this category.

The chemistry of fluorine showed a rather slow growth prior to World War II. The primary problems were related to its reactivity and to the need for proper materials for handling it. As a result of technological development during the war, however, this barrier was overcome, and the field of fluorine chemistry started very rapidly growing and became one of the most active fields in both organic and inorganic chemistry. This growth is symbolized in part by the formation

of a division of fluorine chemistry in the American Chemical Society - one of the few divisions which is built around an element. Such great growth is probably due to the uniqueness of properties which fluoroine compounds tend to display.

The thermochemistry of fluorine showed a parallel rapid growth with a number of laboratories setting up facilities for handling elemental fluorine as a reactant in the calorimetry; and others studying its thermochemistry, but limiting themselves to reactions involving only the combined element. We may refer to the Argonne National Laboratory; the Fulmer Research Institute in England, John Margrave's laboratory at Rice University; and the NBS laboratories, as examples of places where elemental fluorine could be handled. Both flow calorimetry and bomb calorimetry can be carried out in the NBS laboratories.

The use of reactions of fluorine compounds in which the element is never free has a longer history in calorimetry; and in fact the use of hydrofluoric acid solution calorimetry has played an important role in the thermochemistry of silicates and other mineral products for many years. However, application of bomb calorimetry to reactions involving aqueous HF has awaited the development of the rotating-bomb calorimeter.

Among the fluorine compounds there are many that have interesting features. There is one, however, that is almost omnipresent in the thermochemistry of fluorine - that is, hydrogen fluoride, either as the gas or as its aqueous solution, hydrofluoric acid. This compound has a complexity of its character, in particular the large degree of hydrogen bonding that it exhibits, which renders it a fit subject for investigation of many of its properties; but the feature which attracts our attention is its occurrence in so many reactions of fluorine compounds. For the chemistry of fluorine it has an importance analogous to the importance of water in the chemistry of oxygen.

In the thermochemistry of fluorine as in the chemistry of fluorine the acid or its aqueous solution occur in many processes that have been studied. As a result, the actual values that are derived for the heats of formation of various compounds are dependent on the value assigned to the heat of formation of hydrogen fluoride.¹

A few examples are shown below of processes typical of those by which the thermochemistry of fluorine has been derived. These should be multiplied a hundredfold to give the true importance of the compound in this area.

¹In this note thermochemical values are given in kcal mol^{-1} as taken from the original literature or recent reviews in which the kcal is equivalent to 4184 J (exactly).

Typical Processes By Which the Thermochemistry
of Fluorine Compounds Has Been Derived

- (1) $\text{C}_2\text{F}_4(\text{solid polymer}) + \text{O}_2(\text{g}) + 42\text{H}_2\text{O}(\text{l}) = 2\text{CO}_2(\text{g}) + 4[\text{HF} \cdot 10\text{H}_2\text{O}] (1)$
- (2) $\text{BeO}(\text{c}) + 2\text{HF}(\text{aq}) = \text{BeF}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- (3) $\text{NaF}(\text{c}) = \text{Na}^+(\text{aq}) + \text{F}^-(\text{aq})$
- (4) $\text{SiF}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) = \text{SiO}_2(\text{cristobalite}) + 4\text{HF}(\text{g})$

We might ask ourselves the question: How precise and accurate do thermochemical values such as heats of formation have to be? This is a question that really has no exact answer. The answers depend upon the purposes to which the data are to be put.

We can give one answer which shows some inadequate values. See Table I.

Table I. Accuracy of Estimates of Heats of
Formation of Some Fluorine Compounds

| Compound | ΔH_f kcal mol ⁻¹ | | Error |
|----------------------|-------------------------------------|-------------------|---------------------------|
| | Estimate | Later Measurement | |
| NbF ₅ (c) | -342 | -432 | +90 |
| PF ₅ (g) | -315 | -381.4 | +66 |
| | -420 | | -39 |
| RuF ₅ (c) | -300 | -213.4 | -87 |
| SF ₄ (g) | -156 | -171.7 | +16 |
| TaF ₅ (c) | -300 | -455 | +155 |
| | -360 | | +95 |
| Average error | | | 44 kcal mol ⁻¹ |
| Average bias | | | 26 kcal mol ⁻¹ |

Estimates are selected from a review by Armstrong and Krieger [1].

In a recent review of the thermochemistry of fluorine compounds [1]* we came across a number of compounds for which estimates of heat of formation had been made at a time there was no available measured value. The values that have been measured thereafter in some thirty cases were compared with the estimates. A sampling of the results, recently updated, is shown in Table I. The average error was 44 kcal mol⁻¹; the average bias was 26 kcal mol⁻¹. While it is not easy to say what is adequate accuracy; we would contend that this is not accurate enough for anything but the roughest work.

If one is trying to make equilibrium calculations, one should realize that an uncertainty of 1 kcal mol⁻¹ in a heat of formation can lead, at room temperature, to an uncertainty of a factor more than 5 in its equilibrium concentration.

If one is trying to correlate bond lengths and strengths or determine changes in strain energies, a kilocalorie may be adequate for some cases, but for others a much smaller uncertainty is needed. If one is trying to carry out a Hess' law calculation that involves adding a number of reactions, one may want considerably better values.

We are dealing, in the case of hydrogen fluoride, with uncertainties of the order to 0.5 kcal mol⁻¹. To some who would be satisfied with the 1 or 2 kcal mol⁻¹ our discussion may seem to be nitpicking. On the other hand, to those who are accustomed to the idea that the heat of formation of water has an uncertainty of about 0.01 kcal mol⁻¹ this seems inadmissibly large.

II. Flame Calorimetry of Reactions Forming HF(g)

Several early calorimetric measurements of the energy of the reaction of the elements were used to arrive at the heat of formation of gaseous HF. A later reaction involving the combustion of ammonia suffers the same problems. These are shown in Table II.

There are two problems. The first is the problem of corrosion and accounting for all of the reaction products. The second which is a major one is the question of the non-ideality of gaseous HF has been the subject of several studies none of which is definitive in the lower pressure region near room temperature. The gas undergoes polymerization, forming significant quantities of H₂F₂, H₃F₃, H₄F₄, H₆F₆, even at pressures of less than one atmosphere.

Figure 1 shows the quantity Z as a function of pressure along several isotherms. The quantity Z has the value 1 for an ideal gas. Note in the figure that it deviates from unity even at very low pressures.

* Figures in brackets indicate the literature references on pages 14-16.

We are not prepared here to discuss all the PVT data, not all of which is shown here. Two or three sources but by no means all of them have been used in deriving the graph. It will be noted that the data from different sources are significantly different along several isotherms. Also of some importance is the fact that the data are incomplete at the very low pressure end, even though Z still deviates from unity. This lack of completeness has caused some difficulty in extrapolation. A model of the polymerization is necessary and the number of possible polymers renders the interpretation of such a model in the light of the available data somewhat ambiguous.

Figure 2 gives the parameter most interesting to us that can be derived from the PVT data, $H^\circ - H$

$$\text{Remembering that } H^\circ_{298} = H_{298} + (H^\circ_{298} - H_{298})$$

we see from the figure that the enthalpy of the ideal gas differs from that of the real gas by several tenths of a kilocalorie per mole in this region. The solid lines represent values calculated from the work of Long, Hildebrand, and Morell [8]. The dashed lines represent the work of Strohmeier and Briegleb [9]. Note that these differ by a factor of two in this region. Medvedev [7] in 1963 made a recalculation of the correction for non-ideality based on the heat capacity of the real gas studied by Franck and Meyer [10] and of the ideal gas compiled by Gurevich, et al. [11]. This recalculation shows the non-ideality to be less again by a factor of two than we derived from the work of Briegleb and Strohmeier. In Table II we see several determinations of the heat of formation of HF and effects of corrections based on different interpretations of the non-ideality.

The value of -64.2 for NBS Circular 500 [12] was apparently derived by using the value of Ruff and Laas (as corrected by Ruff and Menzel) or by averaging three of the values shown.

If we refer to figure 2, we see in the inset that at higher temperatures the differences between various non-ideality corrections approach each other and tend to go to zero. Of the various measurements shown in Table II, only the one by von Wartenberg and Schutza was done at a high enough temperature that non-ideality corrections could be ignored. Thus this value is the only really unambiguous value for gaseous HF obtained by direct combination of the elements.

The measurement of the combustion of ammonia in fluorine suffers the same ambiguity as the other measurements.

The value $-64.2 \text{ kcal mol}^{-1}$ selected for NBS Circular 500 was generally accepted and received wide usage. An analysis of the heat of solution, some equilibrium constant data and heat of dilution data led to the heat of formation at a series of aqueous solutions. These values from Circular 500 are shown in Table III.

Table II

Flame Calorimetric Studies of the Heat of Formation of HF(g)

| | $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) = \text{HF}(\text{g})$ | | ΔH_f° 298.15, kcal mol ⁻¹ | |
|---|---|--|---|---------------------|
| | | | Original | Recalc(1) Recalc(2) |
| a | Von Wartenberg and Fitzner (1926) [2] | | -63.0 | -63.8 |
| | Russ and Laass (1929) [3] | | -62.3 | -64.2 |
| | Von Wartenberg and Schutz (100°) (1932) [4] | | -65.45 | -- |
| | $\frac{1}{3}\text{NH}_3(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) = \text{HF}(\text{g}) + 1/6 \text{N}_2(\text{g})$ | | | |
| | Armstrong and Jessup (1960) [5] | | -64.22 | -64.77 |
| | | | -64.63 | |
| | Recalc(1) Ruff and Menzel (1931) [6] | | | |
| | Recalc(2) Medvedev (1963) [7] | | | |

Table III. Some Tabulated Values for $\Delta H_f[\text{HF}]$

| | Ideal gas | 10 H ₂ O | ∞ H ₂ O |
|--------------------------|-----------------|---------------------|---------------------------|
| NBS Circular 500 [12] | -64.2 | -75.605 | -78.66 |
| NBS Tech Note 270-3 [13] | -64.8 | -76.235 | -79.50 |
| JANAF Tables [14] | -64.8 \pm 0.3 | | |
| Cox and Harrop [15] | | -77.247* | -80.43* |

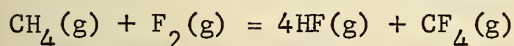
* based on -64.8 for the ideal gas rather than -64.92 as used by Cox and Harrop.

III. Evidence Drawn from Other Reaction Processes

The first inkling the author had of a possible error in the heat of formation of HF came on examining the information collected in the middle and late nineteen fifties on the heat of formation of CF₄.

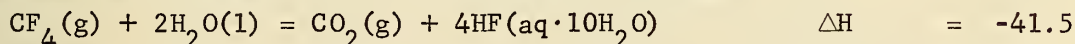
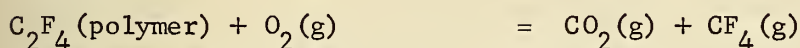
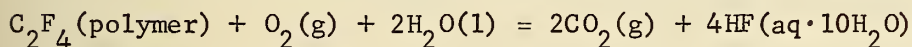
We may illustrate the nature of the clue by the following reactions:

Table IV.



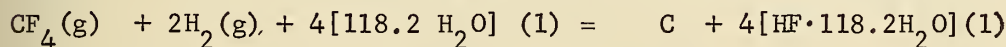
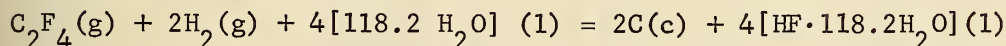
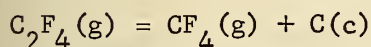
Jessup, McCoskey, and Nelson [16]

Using -64.2 kcal for $\Delta H_f[\text{HF}(\text{g})]$ we get $\Delta H_f[\text{CF}_4(\text{g})] = -220.4$



Good, Scott, and Waddington [17]

Using -75.605 kcal for $\Delta H_f[\text{HF} \cdot 10\text{H}_2\text{O}]$ we get $\Delta H_f[\text{CF}_4(\text{g})] = -218.3$



Neugebauer and Margrave [18]

Using NBS 500 value for $\Delta H_f[\text{HF} \cdot 118.2\text{H}_2\text{O}]$ we get
 $\Delta H_f[\text{CF}_4(\text{g})] = -217.5$

Note that CF_4 and HF appear on the same side in Jessup's reaction and on opposite sides in the other two.

We suggested that the above values could be reconciled if $\Delta H_f^\circ[\text{HF}]$ was in error by a few tenths of a kilocalorie per mole.

A number of other reactions were also available and tended to confirm this view.

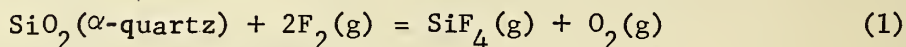
One direction the above suggestion led was to a series of further determinations on $\text{CF}_4(\text{g})$ and another direction was to a new appraisal of the heat of formation of $\text{HF}(\text{g})$ and $\text{HF}(\text{aq})$.

In every case, where the heat of formation of CF_4 and HF were tied together, the above suspicion was further confirmed. It became apparent at least to us, that so long as the uncertainty prevailed in the heat of formation of HF, no reaction involving both HF and CF_4 would be of much assistance in defining the heat of formation of CF_4 . Other methods were sought and were brought successfully to a conclusion, we think.

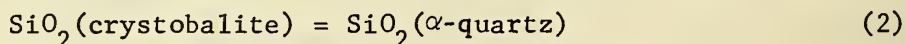
With regard to the heat of formation of HF, a new series of studies was begun. The idea of trying to bring in the results of the relevant data obtained by the new techniques of fluorine bomb calorimetry was seriously proposed by Feder, Hubbard, Wise and Margrave [19]. They immediately derived a value of $-64.92 \text{ kcal mol}^{-1}$ for $\Delta H_f^\circ[\text{HFg}]$.

A typical series of reactions they introduced is shown in Table V.

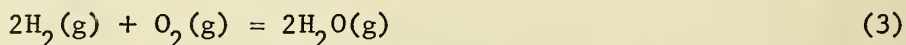
Table V. A Series of Reactions Leading to $\Delta H_f^\circ[\text{HF}(\text{g})]$ by Hess' Law



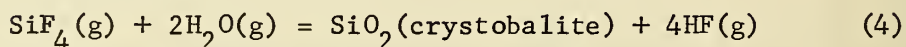
$$\Delta H_{298}^\circ(1) = -168.26 \pm 0.28 \quad [38]$$



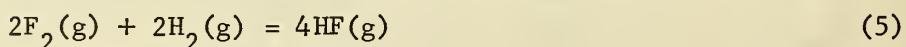
$$\Delta H_{298}^\circ(2) = -0.35 \pm 0.05 \quad [39]$$



$$\Delta H_{298}^\circ(3) = -115.598 \pm 0.020 \quad [12]$$



$$\Delta H_{298}^\circ(4) = +24.53 \pm 0.36 \quad [40, 19]$$



$$\Delta H_{298}^\circ(5) = -259.676$$

$$\Delta H_{f298}^\circ[\text{HF}(\text{g})] = -64.92 \pm 0.12$$

ΔH values are in kcal mol⁻¹, uncertainties are from [19], and are twice the standard deviations of the means.

The revised NBS values (for TN 270-3) by Evans and Parker [13] were prepared about this time and may have been influenced by this value.

There is available one completely different process for calculating the heat of formation of HF. This is the spectroscopic observation of the dissociation of HF.

Table VI. The Heat of Formation of HF(g)
From the Dissociation Energies of H₂, F₂, and HF

| | | | $\Delta H_{298.15}^\circ$ kcal mol ⁻¹ | |
|---|--------|---------|---|------|
| H(g) | + F(g) | = HF(g) | -136.10 | [20] |
| $\frac{1}{2}$ F ₂ (g) | | = F(g) | +18.88 | [13] |
| $\frac{1}{2}$ H ₂ (g) | | = H(g) | +52.095 | [13] |
| <hr/> | | | | |
| $\frac{1}{2}$ H ₂ (g) + $\frac{1}{2}$ F ₂ (g) | | = HF(g) | -65.125 | |

The necessary series of reactions is shown in Table VI. Note that the dissociation energy given by the work of Johns and Barrow [20] must be combined with the dissociation energy of fluorine. This may be the limiting step in the process. To illustrate the large amount of information available, we present in figure 3 the measurements uncovered in a review [1] of the work reported on this limited subject in a period of some 10 years following the issuance of NBS Circular 500. Distilled out of this mass of work, we find almost the only work upon which the current best value rests follows the analysis of Stamper and Barrow [21] (Figure 4), who obtained the dissociation energy from a 3rd law correlation of the experimental work of Wise [22] and of Doescher [23]. As you can see from the boundary lines, almost full weight was given to the work of Doescher. This has become a textbook example of the analysis of equilibrium data by the third law of thermodynamics. The figure, from Stamper and Barrow, was found in Pitzer and Brewer (Lewis and Randall) [24].

Note that the uncertainty (0.01 ev. or 0.23 kcal) assigned by the authors to the dissociation energy of HF would just about overlap the value currently accepted for HF (TN 270-3). In order for an error in the value assigned to the dissociation of F₂ to bring the ΔH_f into line would require a slightly larger dissociation energy of F₂ than we get from Stamper and Barrow's analysis.

IV. Recent Work on the Energy of Vaporization from Water

One of the more important contributions that came out following the revival of interest in HF was a series of reactions leading to the heat of solution of HF in H_2O by Cox and Harrop [15]. This threw a real monkey wrench into the situation. These reactions are found in Table VII.

The series of reactions was rather long, but each step was very small (except for the vaporization step). The series was planned in such a way as to allow no contribution from the non-ideality of the HF gas.

The value shown in Table III for $10\text{H}_2\text{O}$ was obtained from this sum of reactions, by merely adding to the heat of formation of HF(g) as listed for TN 270-3 [13].

The difficulty is that this is now a whole kilocalorie per mole more negative than had been selected for TN 270-3 which was already 0.63 or more kcal more negative than had been listed in NBS Circular 500 [12].

We have looked carefully over the work of Cox and Harrop for a source of discrepancy and so far certainly nothing positive has been discovered. We naturally turn to the largest term - the vapor pressure point. To get one kcal mol^{-1} by an error here would require the pressure to be in error by a factor of five, and even 0.4 kcal would require an error of a factor of two.

One tantalizing prospect is that there is an error in the calculation of ΔS for the reaction. Now S for HF(g) can be calculated quite accurately, and $S_{298} - S_0$ for LiF and LiHF_2 have both been measured in very reliable laboratories. If S_0 is zero for all substances, there hardly seems to be a chance for an error in calculating ΔS .

The possibility of a residual entropy for LiF seems hardly conceivable. The possibility of a residual zero point entropy for $\text{LiHF}_2(\text{c})$ seems not so far fetched - and this reminds us of the classical thermodynamic problems in the verification of the third law of thermodynamics.

Table VII. Cox and Harrop Study of HF(aq)

| | ΔH_{298}° kcal mol ⁻¹ |
|---|--|
| (+) $\text{LiHF}_2(\text{c}) + 6017 \text{ H}_2\text{O}(\text{l}) = [\text{LiHF}_2 \cdot 6017 \text{ H}_2\text{O}](\text{l})$ | $1.860 \pm 0.038^{\text{a}}$ |
| (-) $\text{LiF}(\text{c}) + 6008.67 \text{ H}_2\text{O}(\text{l}) = [\text{LiF} \cdot 6008.67 \text{ H}_2\text{O}](\text{l})$ | 1.059 ± 0.028 |
| (+) $[\text{HF} \cdot 8.33 \text{ H}_2\text{O}](\text{l}) + 6008.67 \text{ H}_2\text{O}(\text{l}) = [\text{HF} \cdot 6017 \text{ H}_2\text{O}](\text{l})$ | -0.740 ± 0.006 |
| (-) $[\text{HF} \cdot 8.33 \text{ H}_2\text{O}](\text{l}) + [\text{LiF} \cdot 6008.67 \text{ H}_2\text{O}](\text{l}) =$ $[\text{LiHF}_2 \cdot 6017 \text{ H}_2\text{O}](\text{l})$ | -0.177 ± 0.006 |
| (-) $\text{LiHF}_2(\text{c}) = \text{LiF}(\text{c}) + \text{HF}(\text{g})$ | 13.410 ± 0.048 |

$$\text{HF}(\text{g}) + 6017 \text{ H}_2\text{O}(\text{l}) = [\text{HF} \cdot 6017 \text{ H}_2\text{O}](\text{l}) \quad -13.172 \pm 0.068$$

^aUncertainties are twice the standard deviation of the mean, assigned by Cox and Harrop.

We have here a very strong hydrogen bond (FHF^-). The question of the zero point entropy in salts containing the bifluoride ion has been the subject of numerous investigations. Westrum [25] did his thesis with Pitzer on this very subject (KHF_2) and satisfied himself by a thermodynamic cycle involving the heat capacity and vapor pressure of KHF_2 and the heat capacities of KF and HF that the proton is not assymmetric. Other evidence is from structural analysis (neutron diffraction) (F-F distance) and from the infrared spectra of the salts. No positive evidence for an unsymmetrical hydrogen bond has been reported for KHF_2 , KDF_2 , NaHF_2 . In the H_2F_3^- ion the protons are assymmetric as would be expected.

The evidence actually put forward on LiHF_2 is too limited to draw any conclusions specifically for it, the only direct evidence being a measurement of the F-F distance, which turns out to be only slightly greater than in KHF_2 .

Table VIII. Vapor Pressure of HF Over $\text{LiHF}_2(\text{c})$.

Effect of a Zero-Point Entropy of $\text{LiHF}_2(\text{c})$

$$\text{LiHF}_2(\text{c}) \rightarrow \text{LiF}(\text{c}) + \text{HF}(\text{g}) \quad P_{298} = 1.89 \pm 0.14^a \text{ Torr}$$

$$\Delta G^\circ = -RT \ln P = 3.553 \pm 0.044 \text{ kcal mol}^{-1}$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

| with | S_{298}° | and assuming S_0° | or S_0° |
|---------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| | $\text{cal deg}^{-1} \text{mol}^{-1}$ | $\text{cal deg}^{-1} \text{mol}^{-1}$ | $\text{cal deg}^{-1} \text{mol}^{-1}$ |
| HF(g) | 41.51 ± 0.01^a | 0 | 0 |
| LiF(c) | 8.52 ± 0.04 | 0 | 0 |
| $\text{LiHF}_2(\text{c})$ | 16.97 ± 0.04 | 0 | 1.38 (R ln 2) |
| | | ΔS | ΔS |
| ΔS | , kcal mol^{-1} | +33.06 | 31.68 |
| $T\Delta S$ | , kcal mol^{-1} | 9.857 | 9.445 |
| $\Delta H_{298.16}^\circ$ | , kcal mol^{-1} | 13.410 | 12.998 |

Uncertainties given are estimated as twice the standard deviation of the mean.

If the proton were assymetric we would expect $R \ln 2 \pm 1.38$ for S_0 of LiHF_2 and this would lead to a slightly lower enthalpy of vaporization and a slightly less negative heat of formation of HF (by 0.4 kcal mol^{-1}). See Table VIII.

The possibility of this is reduced further by the fact that a Clausius-Clapeyron calculation of the heat of vaporization of HF from LiHF_2 by Westrum and Burney [26] give $13.7 \text{ kcal mol}^{-1}$, which is even larger than the vaporization energy given by Cox and Harrop. The work on the (FHF^-) bond was recently summarized in an informal report by the author [27].

V. Heat of Formation of Aqueous HF-Recent Studies

More recently evidence has begun to accumulate concerning the heat of formation of aqueous HF, drawn from completely independent sources.

In Figure 5 we show as the lower line the heat of formation of $\text{HF}(\text{aq})$ as a function of $\text{H}_2\text{O}/\text{HF}$ ratio, as listed in TN 270-3 [13]. In the upper curve are shown the results of Cox and Harrop [15]. In between are points representing the heats of formation as found from more recent data. Typically these points are derived from the heat of

formation of a fluoride by direct combination of the elements or some other process; combined with a hydrolysis reaction in which HF(aq) is formed. The points are located at the concentration of HF(aq) that was actually formed experimentally. We find definite evidence of a "concensus" that the heat of formation of HF(aq) must lie between the two extremes represented by the upper and lower curves.

These data come from several laboratories. The two BF_3 points (points 1 and 2) represent direct combinations of boron and fluorine as measured at NBS [28] and at Argonne [29], combined with a cycle for the hydrolysis of BF_3 proposed by Hubbard [29]. The three CF_4 points (points 3, 4, and 5) represent the recent determination of the heat of formation NPL [31] and Wisconsin [18]. This could be augmented by a very similar pair of points based on work on CF_4 at Argonne [32]. The NF_3 point was performed completely at Dow Thermal Laboratory [33]. The HF point (point 7) was by directly forming the solution from the elements and water (by King) in our laboratories [34]. The latter point if combined with the heat of solution of HF from TN 270-3 [13] leads to $\Delta H_f(\text{HF(g)}) = -65.15 \text{ kcal mol}^{-1}$. Similar values would also be found from other data points in Figure 4.

One final piece of work may be mentioned in closing. Rodenberg and Vanderzee [35] have recently completed a measurement of the heat of solution of HF in NaOH solution leading to the heat of formation of fluoride ion or of HF at ∞ dilution. By their calculation they find ΔH_f at $\infty \text{ H}_2\text{O}$ is in agreement with the value in TN 270-3. Because the extrapolation to ∞ dilution is several kilocalories per mole this is not necessarily inconsistent with the finding shown in the chart. If confirmed, however, it could mean that the dilution energy (to ∞ dilution) is in error.

The recent review by D. R. Stull and collaborators [36] summarizes in a systematic way much of the material presented above, possibly including some additional material. The validity of such a summary, and the enthalpy of formation derived from it depend strongly upon the weights assigned to the various contributing reactions.

VI. New Work on the Dissociation of F_2 and HF

An important very recent contribution to this subject is made by Dibeler, and co-workers [37] who have measured the dissociation energy of fluorine and of HF . Note that if their two values are taken together, the enthalpy of formation of HF(g) can be calculated, in the same way as in Table VI, and give a value in good agreement with values cited above. However, if their F_2 dissociation energy is combined with the dissociation energy of HF reported by Johns and Barrow [20] a discrepancy of about 3 kcal mol^{-1} is found. This is rather substantially outside the limits suggested by the large aggregation of data on HF(g) given above. A very real problem arises as a result of the new work. If the calorimetric thermochemistry be taken as conclusive evidence of

an enthalpy of formation of HF(g) of -64.8 ± 0.5 kcal mol⁻¹, and the work of Dibeler and co-workers be accepted, then an error must be present in the analysis of Johns and Barrow, which is unexpected in view of the very fine consistency of the results they obtained, or as suggested by Dibeler, et al., they have measured vibrational levels above the thermodynamic dissociation level of HF. A further result of the work of Dibeler, et al., is that bond energies calculated on the basis of the dissociation energy of F₂ will be appreciably lower than previously calculated.

VII. References

- [1] G. T. Armstrong and L. A. Krieger, Progr. Intern. Res. Thermodyn. Transport Properties 1962, 8-77.
- [2] H. von Wartenberg and O. Fitzner, Z. anorg. u. allgem. Chem. 151, 313-25 (1926).
- [3] O. Ruff and F. Laass, Z. anorg. u. allgem. Chem. 183, 214-22 (1929).
- [4] H. von Wartenberg and H. Schuetza, Z. anorg. u. allgem. Chem. 206, 65-72 (1932).
- [5] G. T. Armstrong and R. S. Jessup, J. Research Nat'l Bur. Standards 64A, 49-59 (1960).
- [6] O. Ruff and W. Menzel, Z. anorg. u. allgem. Chem. 198, 375-82 (1931).
- [7] V. A. Medvedev, Zh. Fiz. Khim. 37 (6), 1403-6 (1963).
- [8] L. H. Long, J. H. Hildebrand, and W. E. Morrell, J. Am. Chem. Soc. 65, 182-7 (1943).
- [9] W. Strohmeier and G. Briegleb, Z. Elektrochem. 57, 662-7 (1953).
- [10] E. U. Franck and F. Meyer, Z. Elektrochem. 63, 571-82 (1959).
- [11] L. V. Gurvich, G. A. Khachkuruzov, and V. A. Medvedev, et al., Thermodynamic Properties of Individual Substances 1962, Vols. I, II.
- [12] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, Natl. Bur. Standards Circular 500 (U. S. Government Printing Office, Washington, D. C., 1952).
- [13] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Selected Values of Chemical Thermodynamic Properties, Nat'l Bur. Standards Tech. Note 270-3, January 1968 (U. S. Government Printing Office, Washington, D. C. 20402).

- [14] Dow Chemical Company. JANAF Thermochemical Tables. PB168370; Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia.
- [15] J. D. Cox and D. Harrop, Trans. Faraday Soc. 61, 1328-37 (1965).
- [16] R. S. Jessup, R. E. McCoskey, and R. A. Nelson, J. Am. Chem. Soc. 77, 244-5 (1955).
- [17] W. D. Good, D. W. Scott, and G. Waddington, J. Phys. Chem. 60, 1080-9 (1956).
- [18] C. A. Neugebauer and J. L. Margrave, J. Phys. Chem. 60, 1318-21 (1956).
- [19] H. M. Feder, W. N. Hubbard, S. S. Wise, and J. L. Margrave, J. Phys. Chem. 67, 1148-50 (1963).
- [20] J. W. C. Johns and R. F. Barrow, Proc. Roy. Soc. (London) A251, 504-18 (1959).
- [21] J. G. Stamper and R. F. Barrow, Trans. Faraday Soc. 54, 1592-4 (1958).
- [22] H. Wise, J. Chem. Phys. 20, 927 (1952); J. Phys. Chem. 58, 389-91 (1954).
- [23] R. N. Doescher, J. Chem. Phys. 19, 1070-1 (1951); 20, 330-4 (1952).
- [24] K. S. Pitzer and L. Brewer (G. N. Lewis and M. Randall), Thermodynamics, (McGraw Hill Book Co., 1961).
- [25] E. F. Westrum, Jr., and K. S. Pitzer, J. Am. Chem. 71, 1940-48 (1949).
- [26] E. F. Westrum, Jr., and G. A. Burney, J. Phys. Chem. 65, 344-8 (1961).
- [27] G. T. Armstrong, Nat'l Bur. Standards, Informal Report, July 1966.
- [28] E. S. Domalski and G. T. Armstrong, J. Research Nat'l Bur. Standards 71A, 195-201 (1967).
- [29] G. K. Johnson, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 70, 1-6 (1966).
- [30] E. S. Domalski and G. T. Armstrong, J. Research Nat'l Bur. Standards 71A, 105-117 (1967).
- [31] J. D. Cox, H. A. Gundry and A. J. Head, Trans. Faraday Soc. 61, 1594-1600 (1965).

- [32] E. Greenberg and W. N. Hubbard, J. Phys. Chem. 72, 222-227 (1968).
- [33a] G. C. Sinke, J. Chem. Eng. Data 10, 295-6 (1965).
- [33b] L. C. Walker, J. Phys. Chem. 71, 361-3 (1967).
- [34] R. C. King and G. T. Armstrong, 72A, 113-131 (1968).
- [35] C. E. Vanderzee, Private communication, July 17, 1968.
- [36] A. N. Syverud, AFRPL-TR-69-70, January 1969.
- [37a] V. H. Dibeler and J. A. Walker, Inorg. Chem., Accepted for publication (1969).
- [37b] V. H. Dibeler and J. A. Walker, Private communication, April 1969.
- [38] S. S. Wise, J. L. Margrave, H. M. Feder, J. Phys. Chem. 65, 2157-9 (1961).
- [39] J. P. Coughlin, U. S. Bur. Mines Bulletin 542, (1954).
- [40] F. A. Lenfesty, T. D. Farr, and J. C. Brosheer, Ind. Eng. Chem. 44, 1448-50 (1952).

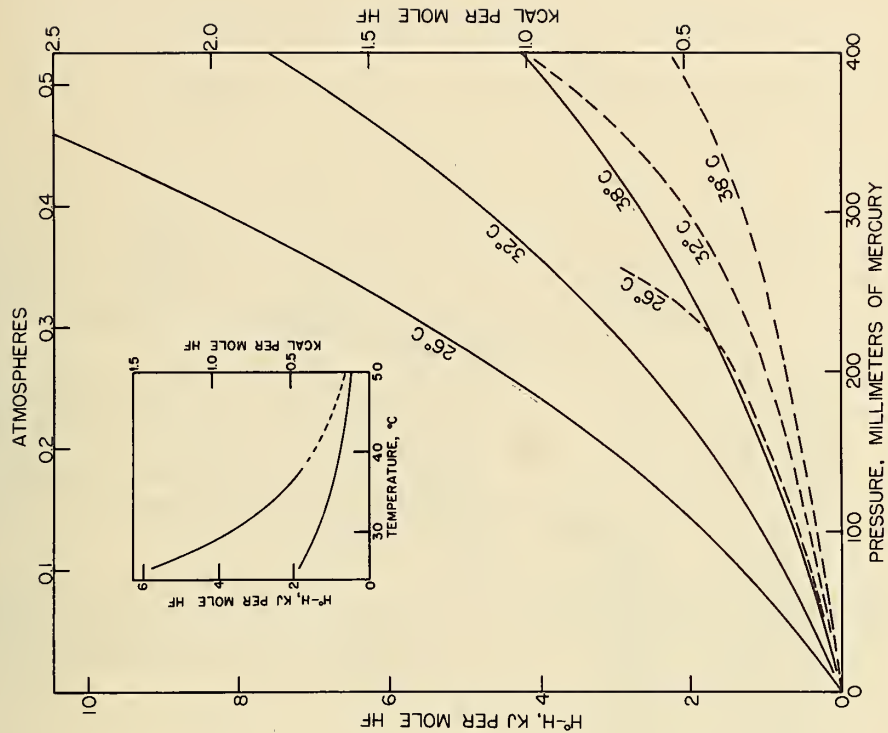


Figure 2

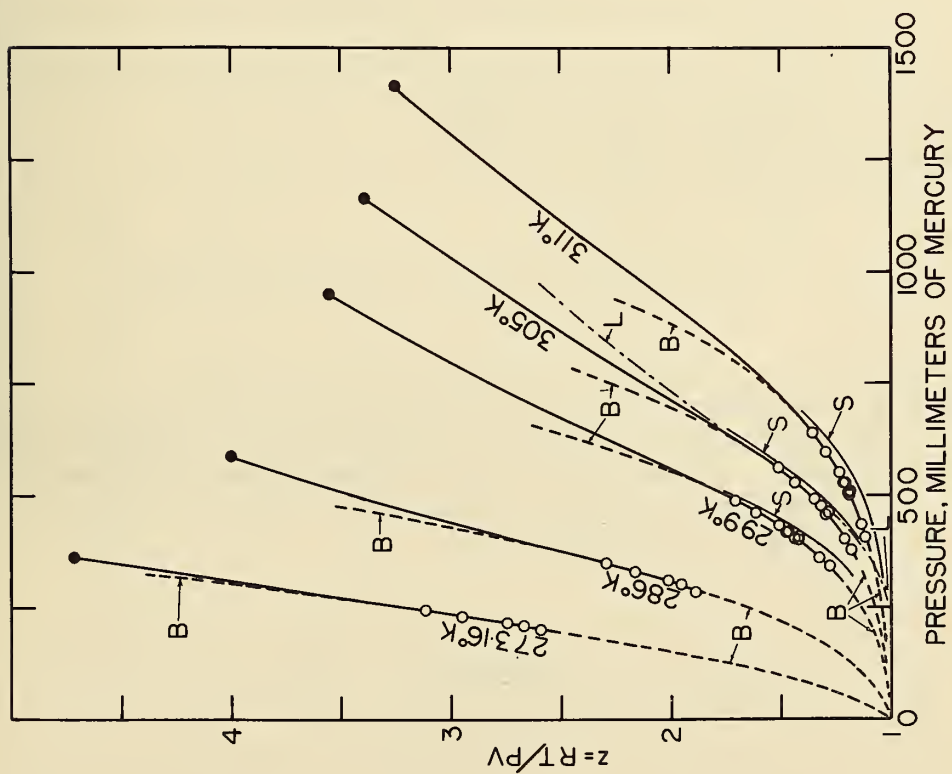


Figure 1

TABLE 1. FLUORINE

| Substance | D_0 or ΔH° (kcal/mole) | Remarks |
|-----------|---|---|
| $F(g)$ | | N.B.S. Circ. 500 [9] gives 18.3 for $\Delta H_f^\circ_{298}$. See $F_2(g)$ for extensive later information. |
| $F_2(g)$ | Experimental measurements leading to D_0 or ΔH° for dissociation have been reported as follows: 66[54], 50 ± 6 [55], < 45 [56], 37.7 at 759 to 1115°K or 38.9 at 1000°K[57], > 45 [58], 40-45[59], 37.7[60], 39.9 ± 0.8 [61], 37.0 ± 2 [62], 31.5 ± 0.9 [63], 37.6 ± 1.6 [64], 37.6 ± 0.8 [65], 31[66,67], 38 ± 0.4 [68, 69], 32 ± 3 [70], 37.5[71], 41.3 ± 0.5 [73], 37.1[92], 31.6 ± 4.3 [606], ≤ 39.0 [606]. | Discussions and calculations of the dissociation energy have been reported by [9, 11, 14, 18, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 89, 90, 91, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 508]. [105] meas. v.p. and ΔH vap. [540] meas. ionization and dissociation by electron impact. [580] est. D_0 values from -34 to +180. |
| $F_2(l)$ | | [105] meas. ΔH fue. |
| $F_2(c)$ | | [105] meas. ΔH trans. (c,I) \rightarrow (c,II). |

Data in tables 1 - 8 are citations from the literature and have not been critically reviewed for this paper.

All numerical values are in kcal mole⁻¹ unless otherwise specified.

See [9] for additional references prior to 1949.

Superscript a on ΔH_f values for Br and I compounds indicates that such values are based on $Br_2(g)$ or $I_2(g)$ as standard states.

Figure 3. Reproduction of a table listing work published on the dissociation energy of fluorine in the interval about 1950 to 1960. The table is taken from reference [1] and the reference numbers listed refer to the bibliography of reference [1].

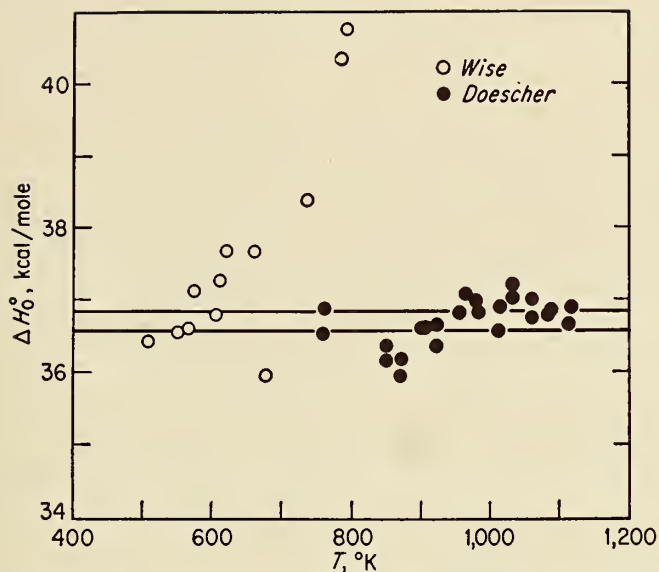


Figure 4 Values of ΔH°_0 of dissociation of F_2 from combination of individual equilibrium measurements with $(F^{\circ}_0 - H^{\circ}_0)/T$ data. [J. G. Stamper and R. F. Barrow, *Trans. Faraday Soc.*, 54, 1592 (1958), fig. 1.]

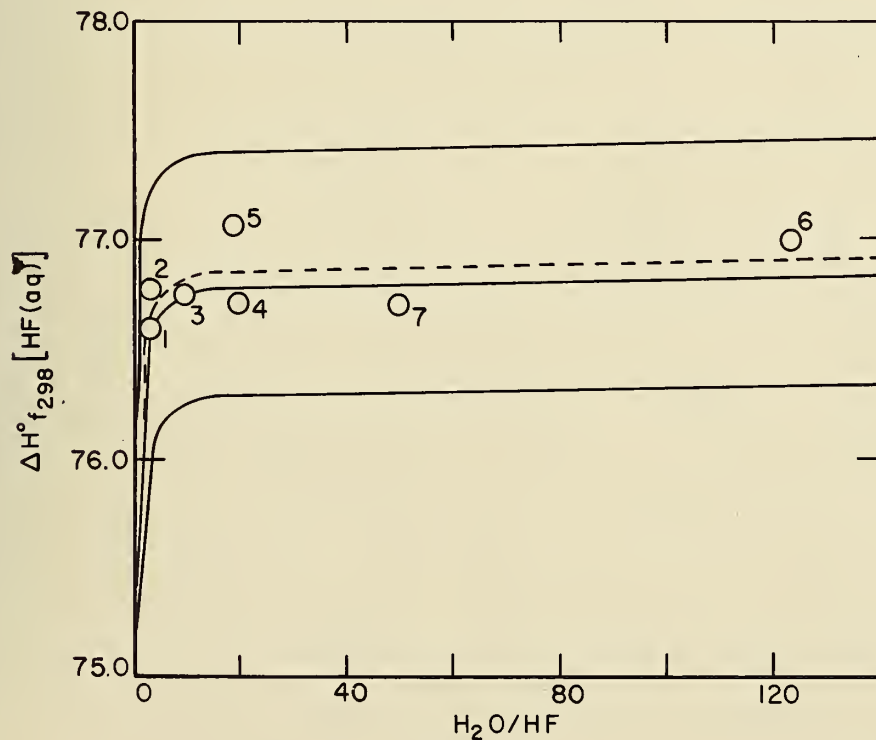
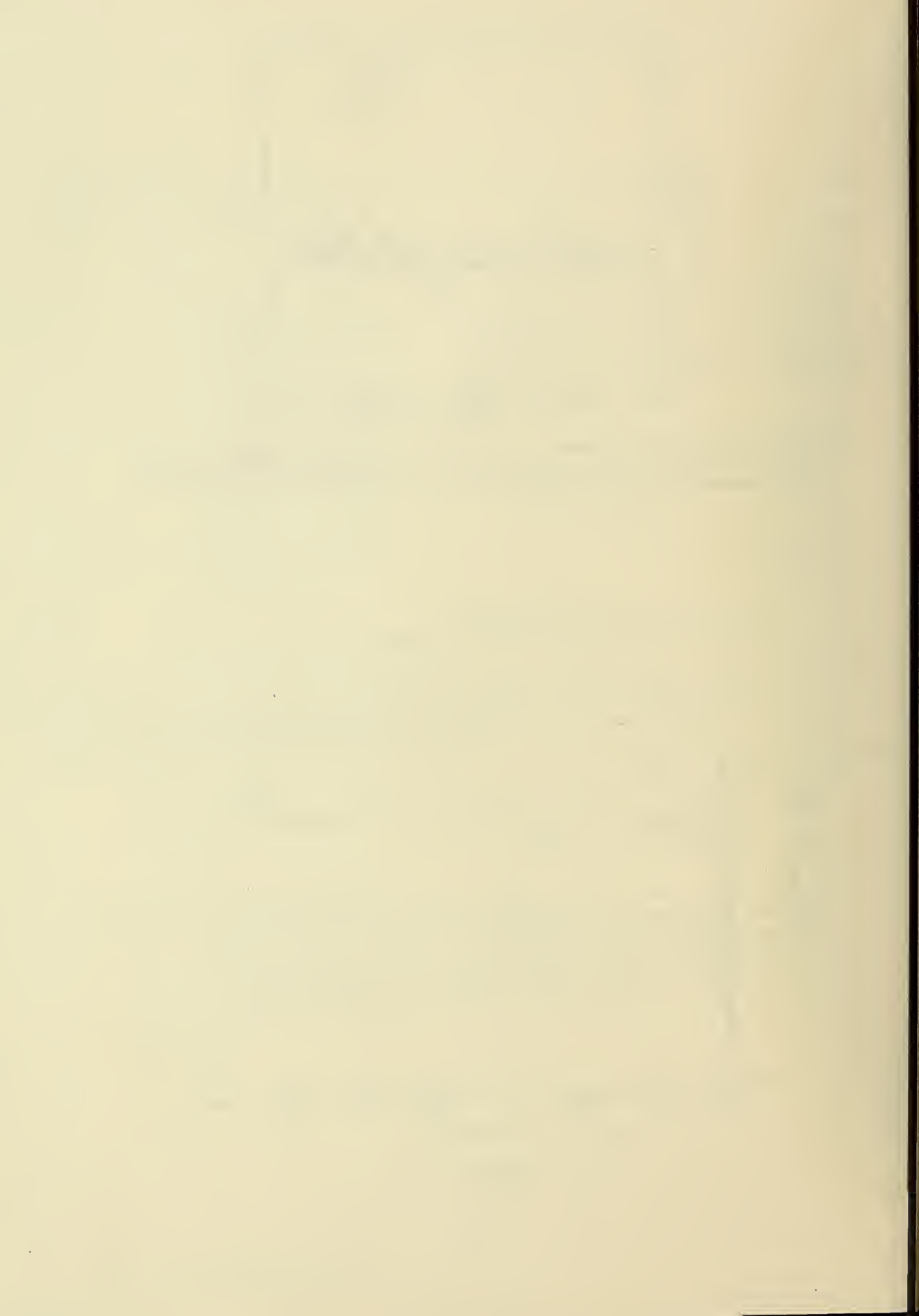


Figure 5



NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

● Physics and Chemistry

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, \$9.50; foreign, \$11.75*.

● Mathematical Sciences

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment; design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, \$5.00; foreign, \$6.25*.

● Engineering and Instrumentation

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, \$5.00; foreign, \$6.25*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—for engineers, chemists, physicists, research managers, product-development managers, and company executives. Annual subscription: Domestic, \$3.00; foreign, \$4.00*.

* Difference in price is due to extra cost of foreign mailing.

Order NBS publications from:

Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

Federal Information Processing Standards Publications. This series is the official publication within the Federal Government for information on standards adopted and promulgated under the Public Law 89-306, and Bureau of the Budget Circular A-86 entitled, Standardization of Data Elements and Codes in Data Systems.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20230

OFFICIAL BUSINESS



POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE
